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Solid Sorbent for Collecting Atmospheric Sulfur Dioxide

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A solid sorbent for collecting atmospheric SO_2 was evaluated as part of an overall effort to develop a replacement method for the West-Gaeke method presently used to measure 24-hour ambient sulfur dioxide concentrations in ambient air. Research showed that a solid sorbent, consisting of Puramer S coated open cell polyurethane foam, can be used to fix the quantities of sulfur dioxide that would be collected if typical ambient air was filtered for 24 hours at 200 cc/min. The method of assaying sulfur dioxide collected by the sorbent consisted of controlled thermal desorption of sulfur dioxide followed by continuous analysis using a Dohrmann microcoulometric titration system. Troublesome sulfur dioxide decay, occurring during post collection storage, was primarily the result of oxidation. Decay was minimized, to an acceptable level, by properly sealing the spent Puramer S collector devices to prevent oxygen contamination from contacting the sorbent prior to thermal desorption and subsequent assaying.

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ABSTRACT

This research program was initiated with the overall objective of developing a replacement method for the West-Gaeke method presently used to measure 24-hour ambient sulfur dioxide concentrations in ambient air.

It was demonstrated that a solid sorbent, consisting of Puramer S coated open cell polyurethane foam, can be used to fix the quantities of sulfur dioxide that would be collected if typical ambient air was filtered for 24 hours at 200 cc/minute.

The method of assaying sulfur dioxide collected by the adsorbent consisted of controlled thermal desorption of sulfur dioxide followed by continuous analysis using a Dohrmann microcoulometric Titration System. Also, it was shown that troublesome sulfur dioxide decay, occurring during post collection storage, was primarily the result of oxidation. This decay was minimized, to an acceptable level, by properly sealing the spent Puramer S collector devices to prevent oxygen contamination from contacting the adsorbent prior to thermal desorption and subsequent assaying.

This report was submitted in fulfillment of 68-02-1782 by Union Carbide Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1, 1975 to November 30, 1977 and work was completed November 30, 1977.

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SECTION 1

INTRODUCTION

One of the goals of the Environmental Protection Agency (EPA) is to accurately monitor 24-hour average sulfur dioxide concentrations in ambient air. This monitoring must be as simple as possible because it is carried out at unmanned monitoring stations where collector pickup is usually performed by unskilled, volunteer workers. The concentration range of interest is 26 to 2600 $\mu g/m^3$ ($\sim$.01 to 1 ppm) for sulfur dioxide.

At the present time, monitoring is generally accomplished using the West-Gaeke method. This wet chemical method uses a toxic liquid collector containing a mercuric salt dissolved in water. This troublesome collector solution is packaged after use and sent to a central testing laboratory for analysis. During both the storage and analysis of spent collectors, spillage can result in unwanted contamination of important work areas. Also, storage at ambient temperatures consistently results in uncontrollable sulfur dioxide decay which leads to lower than actual sulfur dioxide levels. The handling of liquid systems by unskilled workers at the monitoring sites also leads to poor assay accuracy.

The purpose of this investigation, therefore, is to develop a simple, quantitative method for collecting and assaying atmospheric levels of sulfur dioxide. The method is to be based on a proprietary Union Carbide Corporation polymeric amine adsorbent called Puramer S.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that a Puramer S-polyurethane foam adsorbent can be used to fix the levels of sulfur dioxide that would be collected if typical ambient air is filtered for 24 hours at 200 cc/minute. The method of assaying the sulfur dioxide collected by the Puramer S-based adsorbent, consists of controlled thermal desorption of sulfur dioxide followed by continuous sulfur dioxide analysis using a Dohrmann Microcoulometric Titration System.

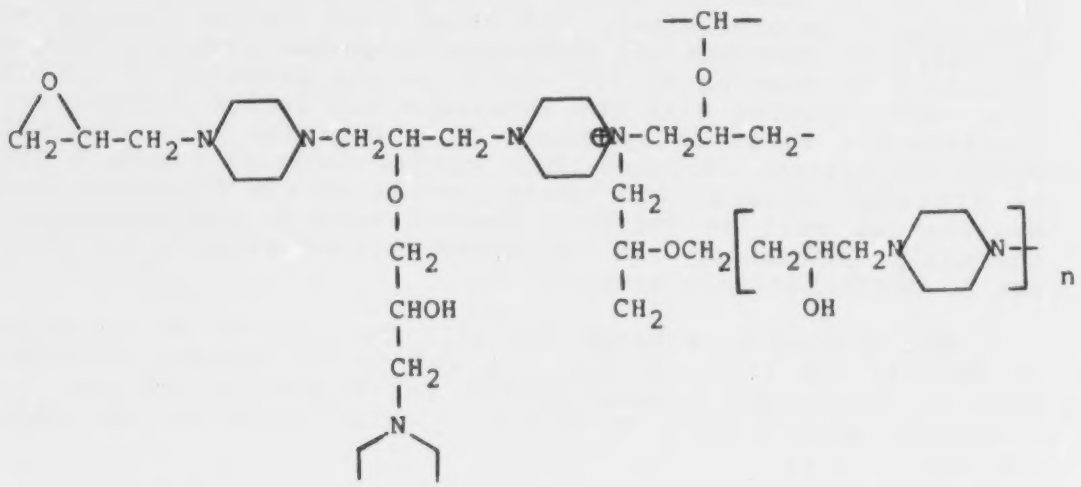
It has also been shown that sulfur dioxide decay can be expected during storage of spent collector devices, but that elimination of oxygen during this storage period reduces the degree of decay to a minimum. Therefore a collector sealing method, based on a glass plug, Teflon sleeve end cap, has been shown to be effective in preventing undesirable sulfur dioxide decay during storage of spent Puramer S collectors at 25°-27°C. Collectors were successfully stored for up to 14 days, prior to assaying, without significant loss of sulfur dioxide (>95% SO_2 recovery). Storage of spent collectors at 40°C were not totally successful. After only 3 days at 40°C, expected assays were reduced by as much as 26 percent. Subsequently, results obtained on spent filters again sealed with the glass rod-Teflon sleeve end cap and stored in an oxygen-free environment showed negligible sulfur dioxide decay. These results indicate the need for an even better collector seal than presently available.

All of the data obtained to date has been under controlled laboratory conditions and free of potential interferences from gaseous species normal to ambient air. Therefore, before this unique Puramer S-based sulfur dioxide monitoring system can be subjected to comparative field study with the presently used West-Gaeke method, a study of possible interferences is recommended. To totally complete the development of the Puramer S monitoring system will require additional funds.

SECTION 3

PRIOR PROGRAM BACKGROUND

As previously mentioned, the sulfur dioxide monitoring system under development is to be based on Puramer S, a proprietary Union Carbide Corporation polymeric amine adsorbent.[1] Puramer S is an efficient, high-capacity sulfur dioxide adsorbent which is prepared by heating N-glycidyl piperazine oligomer until it becomes cross-linked and hence water insoluble.[2,3] It has the following general structure:



PURAMER S

It is the tertiary amine and beta aliphatic hydroxyl groups that are believed responsible for the sulfur dioxide chemisorbent properties of this very unique polymer. Hence, sulfur dioxide is removed from a flowing gas stream as a sulfite or bisulfite group. Because of this chemistry, moisture is very important for efficient sulfur dioxide removal. Best results are obtained at a relative humidity of 70-95 percent.

Early in our UCC Corporate Research funded program, directed towards developing Puramer S adsorbents for use in sulfur dioxide removal from industrial gas streams, as well as ambient air, it was shown that a wide variety of substrates, coated with Puramer S, could quantitatively remove and collect ambient concentrations of sulfur dioxide from properly humidified gas streams, at high linear flow rates.[4] During an ambient air filtration, performed at a New Jersey Environmental Protection Department Air Monitoring Station located in Camden, New Jersey, ambient sulfur dioxide was quantitatively removed using a 2-inch x 1/4-inch Puramer S-polyurethane foam adsorbent, for a continuous period of 70 days.

These results convinced us that low levels of sulfur dioxide could be collected from ambient air and fixed by the Puramer S structure, but we did not know exactly how to measure the collected sulfur dioxide. Early thermal analyses, performed by Dr. B. L. Joesten (Union Carbide Corporation, Research and Development Laboratories), indicated that sulfur dioxide could be thermally desorbed and subsequently purged from the Puramer S structure by heating to 100°-110°C in the presence of nitrogen. This fact, coupled with the knowledge the sulfur dioxide can be continuously measured by means of a Dohrmann Microcoulometric Titration System, dictated that initial contract research should be directed towards the optimization of the Dohrmann Sulfur Analyzer as well as defining thermal methods and equipment for thermally generating the collected sulfur dioxide so that it can be quantitatively assayed.

The following subsections will be devoted to discussing, in detail, the research that has led to the successful development of a Puramer S-based method for measuring the low levels (nanogram quantities) of sulfur dioxide required for ambient air monitoring.

SECTION 4

PURAMER S-BASED AMBIENT AIR MONITORING SYSTEM

Conceptually the Puramer S-based monitoring system consists of two parts: the collector and the analyzer. The collector which is located at the air monitoring site consists of an air mover, probably an air pump, a humidifier to adjust and control the moisture content of the air prior to its entering the Puramer S collector device, a flow controller for adjusting the air flow to 200 cc/minute and finally a Puramer S filter device consisting of two 1-inch by 1/4-inch I.D. plugs of Puramer S-coated polyurethane foam fitted into a 3-inch by 1/4-inch O.D. stainless tube. These collector tubes are prehumidified with enough moisture to assure quantitative sulfur dioxide adsorption during the initial phase of testing. The collector tubes are held in the system by 1/4-inch Swaglok tubing connectors. All connection tubing are made of Teflon or glass. This system is graphically illustrated in Figure 1. After a 24-hour collection cycle, the Puramer S tube is removed, purged with oxygen-free nitrogen and carefully sealed using an oxygen impermeable end cap (probably just a pair of Swaglok tubing caps). This spent collector is sent to a central testing laboratory where the amount of collected sulfur dioxide is assayed.

Presently, this assaying procedure is accomplished using a thermal desorption technique which produces sulfur dioxide at a rate such that continuous gas analysis can be accomplished. The total analysis system consists of an oxygen-free nitrogen purge gas, a gas flowmeter, a Bendix Flasher Unit and a Dohrmann Microcoulometric Titration System, connected in that order. All gas transfer lines are of 1/4 O.D. Teflon tubing and all connections are made with Swaglok tubing fittings. This system is shown in Figure 2. The spent collector is carefully fitted into the Bendix Flasher Unit and collected sulfur dioxide is desorbed by programing the flasher oven temperature from 65°-165°C. The desorbed sulfur dioxide is continuously purged from the collector device, using oxygen-free nitrogen, and assayed via the Dohrmann analyzer. Using this two-part method, sulfur dioxide assays were determined under controlled laboratory conditions (SO_2 loaded via permeation tubes and zero air). As the data in Table I show, excellent results were obtained.

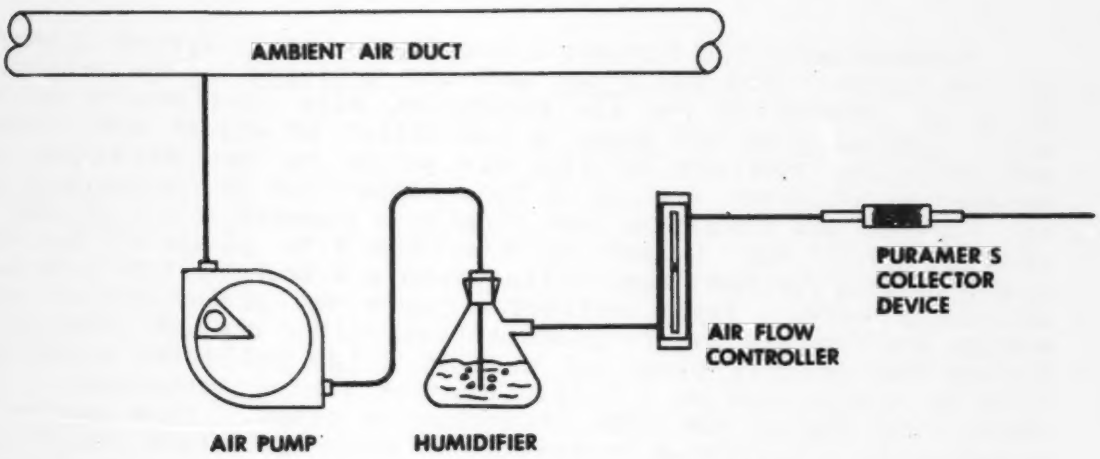


FIGURE 1. PURAMER S BASED SULFUR DIOXIDE MONITORING SYSTEM - COLLECTOR SYSTEM.

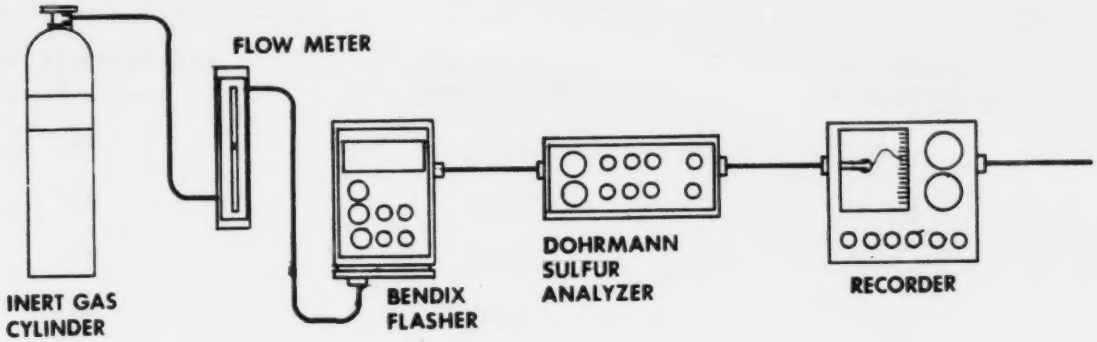


FIGURE 2. PURAMER S BASED SULFUR DIOXIDE MONITORING SYSTEM - ANALYZER SYSTEM.

TABLE 1. SULFUR DIOXIDE ANALYSIS BY A PURAMER S-BASED ANALYTICAL METHOD

Loaded SO_2 - nanograms	Assayed SO_2 - nanograms	SO_2 Recoveries - %
3782	3559	94
4633	4479	97
5254	5233	99
6521	6413	98
9994	9547	96
11138	11288	101
16870	17346	103
17546	17728	101
19385	20208	104
22774	22435	99

It should be mentioned that the total quantities of sulfur dioxide being measured in this study represent analyses of synthetic gas streams, containing sulfur dioxide levels from 13 to 80 $\mu g/m^3$, if collection is carried out for 24 hours at a flow of 200 cc/minute. These sulfur dioxide concentrations are in the range that would be expected in actual ambient air conditions. The accuracy of these results, although obtained under controlled laboratory conditions, certainly demonstrates the feasibility of monitoring ambient levels of sulfur dioxide with a Puramer S-based method.

To bring the Puramer S-based sulfur dioxide monitoring system to its present level of technical development, it was necessary to study many system variables in detail. These studies are individually discussed in the following sections.

SECTION 5

EXPERIMENTAL

SULFUR DIOXIDE ADSORPTION CHARACTERISTICS OF Puramer S - POLYURETHANE FOAM ADSORBENTS

Once it was demonstrated that a Puramer S-polyurethane foam adsorbent could quantitatively collect sulfur dioxide from a properly humidified air stream, it was necessary to determine the proper size adsrobent bed required to assure efficient collection of sulfur dioxide for a minimum of 24 hours at the maximum expected level of ambient sulfur dioxide (2600 $\mu g/m^3$).

To properly size such a Puramer S-based filter, collector devices were prepared by cutting 1-inch x 1/4-inch plugs of adsorbent from foam pieces coated with a wide range of Puramer S concentrations. For test purposes, these adsorbent plugs were fabricated into filter devices by placing them into 6.4 mm I.D., shrinkable Teflon tubing fitted with 3 inch end pieces of 6 mm glass tubing. Using sulfur dioxide loading equipment as described in Section 6.1, Procedures, sulfur dioxide adsorption characteristics of a number of various Puramer S filter devices were determined at a flow rate of 200 cc/minute and a sulfur dioxide concentration of 3590 $\mu g/m^3$. During these evaluations, the water content of the feed gas stream was maintained at approximately 22 mg H_2O/l of air.

As the data in Table 2 show, collection efficiency, defined as the percentage of incident sulfur dioxide removed by the adsorbent, was 100 percent regardless of filter length or the amount of active polymer contained on the foam adsorbent. However, the total collection time for which quantitative removal of sulfur dioxide was realized, was dependent on the particular adsorbent tested. At least 2 inches of foam adsorbent, containing a minimum of 8.6 percent Puramer S will be required if 3590 μg SO_2/M^3 of air is to be collected at 200 cc/minute for a minimum of 24 hours.

TABLE 2. ADSORPTION CHARACTERISTICS OF PURAMER S-POLYURETHANE FOAM ADSORBENTS

Test. No.	Filter Length	Contained Puramer S	Collection Efficiency*	Collection Time**
1	2"	2.0%	100%	7 hrs.
2	1"	8.6%	100%	15 hrs.
3	2"	8.6%	100%	26 hrs.
4	2"	8.6%	100%	28 hrs.
5	2"	8.6%	100%	32 hrs.
6	2"	18.3%	100%	68 hrs.

*Based on the percentage of incident SO_2 removed.
**Time at which zero SO_2 is measured in the filtered effluent gas (less than 7 $\mu g/m^3$).

***Test Conditions:
1. Flow Rate - 200 cc/minute.
2. SO_2 Conc. - 3590 $\mu g/m^3$ in zero air.
3. Relative Humidity - ~85% at 27°C.

Since actual ambient sulfur dioxide levels will be less than 3590 μg SO_2/M^3 of air, a collector device consisting of 2 inches of foam adsorbent, coated with a minimum of 9 percent active polymer, will be more than is required for 24-hour collection cycles. Therefore, future laboratory efforts will center around adsorbents containing at least 9 percent active polymer.

Also, it should be pointed out that tests numbers 1, 3 and 4 were run at 0, 23 and 48 days after the foam adsorbent was prepared. As the data in Table 2 show, storage of Puramer S-based adsorbent, prior to its use as a sulfur dioxide collector, does not affect its overall collection efficiency and within experimental error, does not significantly reduce collection times.

EFFECT OF DESORPTION TEMPERATURES ON SULFUR DIOXIDE RECOVERIES

Having shown that properly sized Puramer S-polyurethane foam adsorbents can quantitatively collect sulfur dioxide from air, efforts were directed towards developing an analytical method for measuring the actual amount of collected sulfur dioxide. As previously mentioned, this assaying method was to be the result of controlled thermal desorption of sulfur dioxide using a Bendix Flasher and continuous sulfur dioxide analysis via a Dohrmann MCTS (see complete method in Section 6.3, Procedures).

As the data in Table 3 show, sulfur dioxide recovery from a Puramer S-urethane foam collector (2 inches long-~12% Puramer S), previously blanked to 170°C to assure that no sulfur dioxide was present prior to loading, was highly dependent on the maximum desoprtion temperature used to produce sulfur dioxide for subsequent assay. At 160°-165°C, recoveries were low and quite

TABLE 3. THE EFFECT OF DESORPTION TEMPERATURE ON SULFUR DIOXIDE RECOVERIES

Loaded SO_2 ng.	Assayed SO_2 ng.	Recovery %	Maximum Desorption Temp., °C
7,217	6,382	88	160°
9,478	6,440	68	165°
19,537	15,040	77	165°
23,485	23,292	99	200°
35,924	34,400	96	190°
4,633	4,479	97	170°*
22,774	22,435	99	170°*

*Purge gas heated to 160°C prior to entering the Bendix Flasher Unit.

variable, while at 190°C and 200°C, recoveries were quantitative. However, being concerned about possible filter decomposition at these high temperatures, which would foul the MCTS cell, attempts were made to reduce the maximum desorption temperature by using preheated purge gas. As the data show, quantitative sulfur dioxide recoveries were realized at 170°C when preheated (∿160°C) gas was employed.

Using a maximum desorption temperature of 170°C, continuous series of sulfur dioxide assays can be run without fouling the MCTS sulfur cell. Until future laboratory studies dictate a change in thermal desorption technique, 170°C will be the final temperature used to regenerate sulfur dioxide for all Dohrmann MCTS analyses.

EFFECT OF PURAMER S CONTENT ON SULFUR DIOXIDE RECOVERY EFFICIENCY

In order to study the effect of Puramer S content (polyurethane foam substrate) on the overall sulfur dioxide recovery efficiencies, using thermal sulfur dioxide desorption and subsequent Dohrmann MCTS analysis, a series of assays were run using 2-inch foam adsorbents containing various amounts of Puramer S. Exact sulfur dioxide loadings were obtained using a calibrated sulfur dioxide permeation tube (see Section 6.1 for a detailed description of the loading method). As the data in Table 4 show, foams containing 4.3 percent and 8.9 percent active polymer gave sulfur dioxide recoveries of 88-91 percent while filters prepared from 12 percent and 18 percent Puramer S foams consistently gave quantitative sulfur dioxide recoveries over a wide range of sulfur dioxide loadings. The data also indicated that higher loadings result in more quantititative recoveries regardless of Puramer S content. It was fortunate that higher loadings resulted in better recovery efficiencies since these and even higher loadings are more realistic, in actual ambient applications, than the lower levels measured in this study.

The poorer recoveries obtained when low Puramer S content adsorbents were tested might be due to sulfur dioxide reaction with the urethane substrate. Using low amounts of active polymer it would be expected that more urethane structure would be exposed to the sulfur dioxide-water than at the higher Puramer S coatings. If sulfur dioxide were to react in such a way as to render the sulfur dioxide stable and no longer thermally regenerable, low recoveries would be realized. More will be said about sulfur dioxide loss due to reaction with the adsorbent in the section discussing adsorbent cycling. Prevention of sulfur dioxide loss by reaction can be achieved using foam coated with at least 12 percent Puramer S.

TABLE 4. EFFECT OF PURAMER S CONTENT ON SULFUR DIOXIDE RECOVERY EFFICIENCY

Puramer S Content	Loaded SO_2 ng.	Assayed SO_2 ng.	Recovery Efficiency
18	4,633	4,479	97
18	22,774	22,435	99
12	3,782	3,559	94
12	4,633	4,479	97
12	6,521	6,413	98
12	9,994	9,547	96
12	16,870	17,346	103
12	17,546	17,728	101
12	22,774	22,435	99
9	3,853	3,387	88
9	5,524	4,855	88
4	3,790	3,335	88
4	6,488	5,917	91

*All Puramer S collectors treated for 5 minutes at 170°C and a 200 cc/minute N_2 purge to assure that no SO_2 wss contained on the adsorbent prior to SO_2 loading.

EFFECT OF COLLECTOR CYCLING ON THE SULFUR DIOXIDE RECOVERY EFFICIENCY

Another parameter that was studied during this laboratory research program was the effect of cycling or re-use of the filters on sulfur dioxide recovery. This study not only showed that reuse was possible, but probably desirable.

Using collector devices containing 2-inch lengths of Puramer S-urethane foam adsorbents, containing 4 percent, 9 percent, and 15 percent active amine polymer, sulfur dioxide was carefully loaded and then analyzed via thermal desorption and subsequent Dohrmann MCTS analysis of the sulfur dioxide in the effluent purge gas (see Sections 6.1 and 6.3 for details of these experimental procedures). After all the collected sulfur dioxide was desorbed and measured, the collector devices were prehydrated by passing moisturized nitrogen ($\sim$22 mg H_2O/ℓ through the device for 5 minutes at 200 cc/minute and the analytical cycle repeated.

The data in Table 5 show that sulfur dioxide recoveries, via thermal treatment, were always lower than expected for the first collection-assay cycle. Once again the recoveries were lowest for adsorbents containing the least amount of Puramer S. In every case, however, second, third and even fourth cycle treatment resulted in quantitative recoveries. Cycling the filters through the desorption part of this process showed that the improved recoveries were not the result of residual sulfur dioxide left on the collector and subsequently measured on the next cycle.

The low, first cycle results again indicated that sulfur dioxide was reacting with some functional group on the adsorbent which renders it nonregenerable and hence, not available for MCTS detection. Once this small amount of reaction was completed, however, the functional group or reactive site was no longer available for sulfur dioxide attack and, therefore, additional cycling resulted in quantitative assays. Efforts will be needed to develop a pretreatment for the Puramer S adsorbent so that quantitative recoveries can be realized in the first cycle. Also, this study showed that EPA could recycle Puramer S collector devicies without affecting subsequent analysis of ambient sulfur dioxide.

TABLE 5. PURAMER S ADSORBENT CYCLING VERSUS SULFUR DIOXIDE RECOVERY EFFICIENCY

Cycle	Puramer S %	Loaded SO_2 ng.	Assayed SO_2 ng.	Recovery %
1	4	6,488	5,917	91
2	4	3,683	3,650	99
3	4	3,452	3,365	98
1	9	3,853	3,387	88
2	9	7,359	7,572	103
3	9	5,557	5,407	97
1	15	24,120	22,320	93
2	15	24,228	23,599	97
3	15	24,084	24,000	100
4	15	24,084	23,441	97

EFFECT OF PREHYDRATION ON THE SULFUR DIOXIDE RECOVERY EFFICIENCY OF PURAMER S ADSORBENTS

Very early in our research, it was shown that many of the low sulfur dioxide recoveries were the direct result of a low moisture content on the Puramer S-polyurethane foam adsorbent prior to sulfur dioxide loading. This was particularly true for Puramer S adsorbents being used to study filter cycling and its effect on recoveries. The low preloading moisture, results in poor adsorption efficiency early in the loading cycle. Because this laboratory effort used short filter loading periods, using high concentrations of sulfur dioxide (3600 μg SO_2/M^3 of air), the effect of moisture on the filter prior to loading was magnified, since there was not enough time, early in the collection cycle, during which water, needed for sulfur dioxide adsorption, could be adsorbed.

As the data in Table 6 show, low sulfur dioxide recoveries due to low pre-sulfur dioxide loading moisture could be easily remedied by simply prehydrating the collectors by passing 200 cc/minute of moisturized nitrogen (∿22 mg H_2O/ℓ) through the device for 5 minutes. (Longer prehydration times did not effect recoveries. Prehydration of Puramer S-based sulfur dioxide collectors is now standard procedure.

TABLE 6. EFFECT OF PREHYDRATION ON THE SULFUR DIOXIDE RECOVERY EFFICIENCY OF PURAMER S ADSORBENTS

Cycle	Puramer S Content	Prefilter Hydration	Loaded SO_2-ng	Assayed SO_2-ng	Recovery - %
7	8.9	No	3,604	2,771	77
8	8.9	Yes	6,587	6,708	102
3	12.0	No	5,016	4,592	91
4	12.0	Yes	19,385	20,208	104

Having completed most of the more important parameter studies, a viable Puramer S-based analytical procedure has been developed. This method can quantitatively assay known amounts of sulfur dioxide which are carefully loaded onto adsorbents under controlled laboratory conditions. The method, however, assumes that actual thermal desorption and subsequent Dohrmann MCTS analysis of the loaded sulfur dioxide is carried out immediately after collection. This is not at all practical because there are sometimes many days that elapse between sulfur dioxide collection and final assay. This delay is caused by shipment of spent collectors from the air monitoring site to a central laboratory for final testing. Before a study of the effect of filter storage time and temperature, after sulfur dioxide collection, on the subsequent recovery efficiency is detailed, a summary of the parameters required to assay sulfur dioxide, by a Puramer S-based method, is appropriate. This summary can be seen in Table 7.

TABLE 7. PURAMER S-BASED SULFUR DIOXIDE ANALYTICAL SYSTEM PARAMETERS

Collection of SO_2
Filter Used - 2" x 1/4" Puramer S-polyurethane foam.
% Puramer S - 12-15%.
Prehydration - Yes.
% Relative Humidity in Gas Stream - 85% at 25°C.
Gas Flow Rate - 200 cc/min.
Assaying of SO_2
Desorption Temp. - 50° to 170°C.
Purge Gas - Oxygen-free nitrogen.
Purge Gas Flow - 135 cc/min.
SO_2 Measurement - Dohrmann MCTS or equivalent.

Using these parameters, sulfur dioxide carefully loaded on Puramer S-polyurethane foam adsorbents can be assayed over a wide range of concentrations. A representative summary of these results are shown in Table 8.

TABLE 8. SULFUR DIOXIDE ASSAYS VIA A PURAMER S-BASED METHOD

24 Hour Average SO_2 Conc.-$\mu g/M^3$	Total Collected SO_2-ng	Assayed SO_2-ng.	SO_2 Recovery - %
13.1	3,782	3,559	94
16.1	4,633	4,479	97
18.2	5,254	5,233	99
22.6	6,521	6,413	98
34.7	9,994	9,547	96
38.7	11,138	11,288	101
58.6	16,870	17,346	103
60.9	17,546	17,728	101
67.3	19,385	20,208	104
78.1	22,500	22,164	99
79.1	22,774	22,435	99
83.6	24,084	23,760	99
83.6	24,084	24,072	100
83.6	24,084	23,280	97
84.1	24,228	23,592	97

EFFECT OF STORAGE ON SULFUR DIOXIDE RECOVERY EFFICIENCY

Having successfully developed a method for assaying ambient levels of sulfur dioxide, collected by a Puramer S-based adsorbent under ideal laboratory conditions, efforts were concentrated on determining whether or not the method was applicable under reallife conditions. The first phase of this study was to determine the effect of storage time and temperature of spent adsorbent (sulfur dioxide loaded), on subsequent recovery efficiency.

Puramer S-polyurethane foam adsorbents were loaded with various amounts of sulfur dioxide using the procedure outlined in Section 6.1. The spent filters were sealed, using rubber septa and stored at 25°-27°C, 45°C, 0°C and -30°C. At various storage times the amount of loaded sulfur dioxide was measured and recovery efficiencies determined. These initial storage data are summarized in Table 9.

These data show that storage of spent Puramer S-based collectors resulted in significant reductions in overall sulfur dioxide recoveries. Sulfur dioxide decay was minimized, to an acceptable level, via sub-zero storage at -30°C. Also, these data showed that the rate of decay was closely related to the storage temperature. At 0°C, 84 percent of the collected sulfur dioxide could be assayed after 21 days of storage while only 33 percent could be found after 24 days at 45°C. Storage at 25-27°C also resulted in a steady loss of sulfur dioxide, with only 68 percent of the collected sulfur dioxide available for measurement after 21 days.

The results seem to suggest that sulfur dioxide was being destroyed via a chemical reaction. It was believed that oxygen present in the free void space of the collector devices could result in oxidation of sulfur dioxide to sulfur trioxide. Sulfur trioxide is not thermally desorbable from Puramer S and if it were, it could not be measured by the Dohrmann analyzer because the sulfur cell employed is specific for sulfur dioxide. Using very simple calculations, it was shown that the 3-inch by 1/4-inch collector tube could contain enough oxygen to convert all the sulfur dioxide, normally loaded, to sulfur trioxide. This contained oxygen could be eliminated via purging with an oxygen-free inert gas, but another calculation[5] quickly showed that air permeation through the rubber septum caps, used to seal the spent collector tubes could allow enough oxygen to enter

TABLE 9. EFFECT OF POST-COLLECTION STORAGE ON PURAMER S ADSORBENT RECOVERY EFFICIENCY

Storage Time-days	Storage Temp.-°C	Loaded SO_2 ng.	Assayed SO_2 ng.	Recovery %
0	25-27	22,774	22,435	99
6	25-27	8,914	7,840	88
0	25-27	16,840	17,346	103
5	25-27	24,214	22,568	93
6	25-27	10,246	8,267	81
26	25-27	31,982	21,600	68
26	25-27	12,794	8,400	66
21	0	25,545	21,360	84
21	0	14,458	11,520	80
21	0	17,424	14,640	84
2	45	13,190	7,680	58
24	45	21,874	7,200	33
2	-30	14,054	15,240	101
3	-30	22,500	22,128	98
6	-30	24,036	23,366	97
12	-30	19,176	18,408	96

the tubes, in 24 hours, to completely convert all the contained sulfur dioxide to trioxide.

Having a full appreciation for the effect of oxygen on the decay of sulfur dioxide fixed on a Puramer S filter, a study was run on spent adsorbents stored at 25°-27°C in an oxygen-free atmosphere. To accomplish this study, spent filters were purged for 10 minutes with oxygen-free nitrogen, again sealed with rubber septa and stored at ambient temperature in a container that was continuously purged with oxygen-free nitrogen. As shown in Table 10, sulfur dioxide decay was reduced by minimizing oxygen during storage. However, some decay still was taking place since only 93-95 percent of the collected sulfur dioxide was measured after 5-7 days.

TABLE 10. PURAMER S--SULFUR DIOXIDE STORAGE STABILITY IN AN INERT ATMOSPHERE

Storage Time-days	Loaded SO_2 -ng.	Assayed SO_2 -ng.	Recovery - %	Storage Atmosphere
0	22,774	22,435	99	Air
6	8,914	7,840	88	Air
26	31,982	21,600	68	Air
1	24,084	22,320	93	Oxygen Free
4	24,144	22,046	91	Oxygen Free
5	24,096	22,800	95	Oxygen Free
7	23,092	21,476	93	Oxygen Free

Again, looking for possible sources of oxygen in our overall test system, it was pointed out that enough oxygen could be dissolved in the rubber end seals, used to cap the spent filters, to convert approximately 38,000 nanograms of sulfur dioxide to undetectable sulfur trioxide.[6] This was more sulfur dioxide than normally collected by the Puramer S adsorbents. These storage studies were very encouraging since they suggested that by using a properly designed collector seal to avoid oxygen contamination, sulfur dioxide decay would be eliminated and spent Puramer S filters would have the required stability, regardless of storage temperature.

A preliminary program to develop an improved seal for spent Puramer S adsorbents, resulted in a seal consisting of

glass rod end butts that were tightly held to the stainless steel collector via small sections of a Teflon sleeve. These seals were firmly held in place using vinyl tape (see Figure 3).

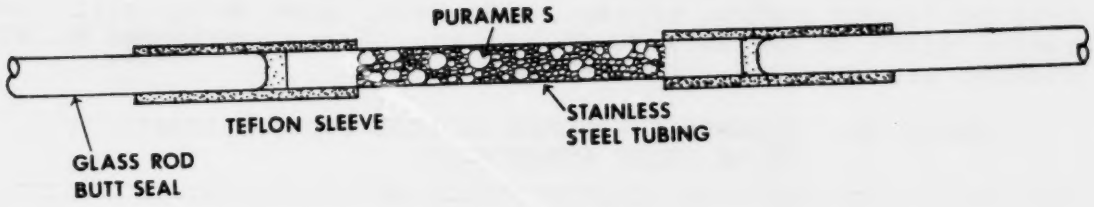


FIGURE 3. PURAMER S FILTER SEAL

These seals were put in place following a 20-minute collector purge with oxygen-free nitrogen. Using filters fitted with these end seals, storage stability tests were run at 25°-27°C for up to 8 days. As the data in Table 11 show, this method of preparing spent collectors for ambient storage proved very effective.

TABLE 11. EFFECT OF PROPER SEALING ON THE STORAGE STABILITY OF SPENT PURAMER S ADSORBENTS

Storage Time -days	Loaded SO_2 -ng	Assayed SO_2 -ng	SO_2 Recovery -%
0	27,704	26,170	94.5
0	23,114	23,117	100.0
0	18,232	18,292	100.3
1	18,521	17,905	96.7
1	18,259	17,753	97.2
3	15,216	14,954	98.3
3	30,772	30,609	99.5
8	20,683	19,532	94.4
8	20,623	19,557	94.8
8	20,472	20,391	99.6

Note--Storage temperature at 25°-27°C.

Although these data show that the glass butt sealing technique was effective for 25°-27°C storage, preliminary results at 40°C indicate that sulfur dioxide decay still occurred at an undesirable rate. Sulfur dioxide recoveries of 88 percent and 74 percent were obtained for sealed collectors stored at 40°C for 1 and 3 days respectively. This decay in recovery was probably due to a small amount of oxygen contamination resulting from the loosening of the end butt seals at 40°C. By placing properly sealed spent filters in sealed jars, that were purged with oxygen-free nitrogen, sulfur dioxide decay due to oxygen contamination was minimized and recovery of 95-98 percent was obtained for a small number of samples.

This finding again suggested the need for a seal that would completely eliminate oxygen contamination of spent filters. Success in developing such an end seal would bring the Puramer S-based sulfur dioxide monitoring method to a point where it would be functional under real-life ambient condition. This final Puramer S-based sulfur dioxide method would eliminate almost all of the troublesome shortcomings of the presently used West-Gaeke method.

SECTION 6

PROCEDURES

METHOD OF LOADING SULFUR DIOXIDE ON PURAMER S ADSORBENTS

A. Purpose:

The purpose of this procedure is to accurately load known amounts of SO_2 on Puramer S adsorbents.

B. Equipment:

1. A calibrated SO_2 permeation tube.
2. A cylinder of zero zir fitted with a properly sized pressure regulator.
3. A cylinder of nitrogen fitted with a properly sized pressure regulator.
4. A constant temperature water bath.
5. A flowmeter and needle valve flow regulator.
6. A glass, U-tube holder fitted with inlet and outlet connectors.
7. Two calibrated thermometers (range 7-31°C).
8. A Dynasciences SO_2 Pollution Monitor fitted with a 0-0.5, 0-1.5, 0-5.0 ppm SO_2 sensor.
9. A 10 mv. strip-chart recorder.
10. 1/4" I.D. Teflon tubing.
11. 1/4" nylon tubing fittings.
12. Two, Drechsel gas washing bottles. (S.G.A. JB-1370.)

C. Equipment Setup: Puramer S Adsorbent Prehydrator.

1. The prehydrator consists of a cylinder of nitrogen, fitted with a properly sized pressure regulator that is connected to a gas flowmeter-regulator using 1/4" I.D. Teflon tubing. The flowmeter-regulator is connected to a 250 ml, Drechsel gas washing bottle containing approximately 200 ml of distilled water, again using 1/4" I.D. Teflon tubing. The off-side of the gas washing bottle is fitted with a 1/4" nylon tubing fitting into which is placed the device containing the Puramer S-based adsorbent.

2. Using a gas flow of 200 cc/minute, moisture is loaded onto the adsorbent for 5 minutes.

D. Equipment Setup: Puramer S Adsrobent SO_2 Loading System.

1. The SO_2 loading system consists of a cylinder of zero air, fitted with a properly sized pressure regulator, a flowmeter-regulator, a 250 ml, Drechsel gas washing bottle containing approximately 200 ml of distilled water, a glass U-tube (containing glass beads in the inlet half and an SO_2 permeation tube and thermometer in the off side) immersed in a constant temperature water bath, a Puramer S adsorbent device holder, a Dynasciences SO_2 Pollution Monitor fitted with a 0-0.5, 0-1.5, 0-5.0 ppm SO_2 sensor and a 10 mv. strip-chart recorder. All of this equipment is connected together, in the order listed, using 1/4" I.D. Teflon tubing and 1/4" nylon tubing fittings.

2. At a constant flow of 200 cc/minute, humidified zero air is passed over a calibrated SO_2 permeation tube ($30° \pm 0.1°C$) until a constant SO_2 concentration is measured by the Dynasciences SO_2 monitor. Once a stable SO_2 concentration is realized, Puramer S adsorbents can be accurately loaded with SO_2 by inserting a Puramer S filter device into the gas stream between the permeation tube and the Dynasciences monitor. By measuring the filtered effluent gas, quantitative collection or removal of SO_2 by the Puramer S adsorbend can be assured. The loading time is recorded by a stopwatch in seconds. The quantity of loaded SO_2 can be varied by varying the loading time. Loaded Puramer S devices are sealed with a proper sealing device.

3. SO_2 Loading = Permeation Rate (ng SO_2/min) x $\frac{\text{Time (sec)}}{60}$

CALIBRATION OF SULFUR DIOXIDE PERMEATION TUBES

A. Purpose:

The purpose of this method is to accurately determine the SO_2 delivery rate of a permeation tube under the exact flow and temperature conditions used when loading SO_2 onto Puramer S adsorbents.

B. Equipment:

1. The exact permeation tube system described in 6.1-D.
2. The SO_2 permeation tube to be calibrated.
3. A Dohrmann Microcoulometric Titration System equipped with a Model T-300P-oxidative sulfur titration cell.
4. 1/4" I.D. Teflon tubing.

C. Equipment Setup and Procedure

1. Using as short a piece of 1/4" O.D. Teflon tubing as possible, connect the exit side of the SO_2 permeation system to the microcoulometric titration cell.
2. Before actually making this connection, set the Dohrmann Microcoulometric Titration System parameters as described in the instruction manual. This usually means a Bias setting of 140-150 ma. and a coulometer gain of 200.
3. After the microcoulometer is properly adjusted, connect the SO_2 permeation system directly to the titration cell and set the permeation conditions of temperature and flow to those to be used in loading Puramer S adsorbents.
4. At a microcoulometer ohm setting of 10, continuously measure the nanograms of sulfur in the synthesized gas stream using the Dohrmann recorder and stroke integrator (each full stroke = 100 counts). Continue this measurement until a stable recorder readout (constant sulfur level in gas) is realized for a minimum analysis period of 30 minutes.

D. Calculation of SO2 Permeation Rate

$$\text{Permeation Rate} = \frac{\text{Total Sulfur Conts} \times 4}{\text{Analysis Time (mins.)}} \times \text{ohm setting}$$

Permeation Rate of SO_2 = nanograms SO_2/minute.

THERMAL DESORPTION METHOD FOR ASSAYING SULFUR DIOXIDE ADSORBED ON PURAMER S-BASED ADSORBENTS

A. Purpose:

The purpose of this method is to quantitatively desorb SO_2 from Puramer S adsorbents so that the SO_2 can be assayed using a Dohrmann Microcoulometric SO_2 Titration System.

B. Equipment:

1. A cylinder of oxygen-free nitrogen, fitted with a properly sized pressure regulator.
2. A Bendix Flasher Unit (Model H/S 10).
3. 3-inch x 0.25-inch stainless steel collector tubes containing Puramer S-polyurethane foam adsorbent (2-inch x 1/4-inch plug).
4. A 25-foot x 1/4-inch O.D. coil of copper tubing filled with small glass beads.
5. A hot plate.
6. A 0-250°C thermometer.
7. A Bell jar containing high-temperature silicon oil stabilized with ionol.
8. A flowmeter.
9. A Dohrmann Microcoulometric Titration System, equipped with a Model T-300P oxidative sulfur titration cell.
10. 1/16-inch O.D. Teflon tubing and stainless steel Swaglok tubing connectors.

C. Equipment Setup:

1. The system used to assay the SO_2 collected on a Puramer S-based adsorbent consists of a cylinder of oxygen-free nitrogen, fitted with a properly sized pressure regulator, a purge gas preheater made up of 25 feet of 1/4-inch O.D. copper tubing filled with glass beads and immersed in a silicon oil bath heated to 160°C via a stirrer-hot plate, a Bendix Flasher Unit (Model H/S 10) and a Dohrmann Microcoulometric Titration System equipped with a Model T-300P oxidative sulfur cell. All parts of the system are connected via 1/16 inch O.D. Teflon tubing using stainless steel Swaglok fittings.

D. Procedure:

1. Using the above described setup, set the nitrogen flow at ∿135 cc/minute.
2. Set the gas preheater temperature at 160°C.
3. With the Bendix Flasher Unit in a gas bypass mode, set the Microcoulometer parameters as per the instrument instruction manual. Set ohm range at 10.
4. Place the spent Puramer S collector device in the Bendix Flasher Oven and set the oven temperature at 50°C.
5. Change the Bendix Flasher Unit to the analysis mode and continuously measure the amount of SO_2 in the collector purge gas.
6. Increase the Bendix Flasher Unit oven temperature in increments of 5°C so as to cause thermal generation of SO_2 at a rate that can be recorded by the SO_2 analyzer.
7. Program the oven temperature to 170°C.
8. Continue the analysis until no more SO_2 is measured (Dohrmann recorder back to the original baseline setting).
9. Cool the Flasher oven to 50°C using compressed air.

E. Calculation of Assayed SO2:

1. Determine the total number of SO_2 integration counts recorded by the disc-integrator.

2. Nanograms SO_2 = $\frac{4 \times \text{total counts}}{\text{ohm setting}}$

3. % SO_2 Recovery = $\frac{\text{assayed } SO_2 \times 100}{\text{loaded } SO_2}$

PREPARATION OF PURAMER S-POLYURETHANE FOAM ADSORBENT AND SUBSEQUENT COLLECTOR DEVICES

A. Materials and Equipment Needed:

1. 45 pores per inch polyurethane foam (Paramount).
2. 15 percent aqueous solution of specification N-glycidyl piperazine oligomer.
3. Vacuum Oven.
4. Buchner funnel and flask.
5. Rubber Dam.
6. Source of vacuum.
7. 8" x 8" x 3" glass dish.
8. Distilled water.

B. Procedure:

1. Cut a 6" x 6" x 1" piece of 45 pores per inch polyurethane foam.
2. Wash thoroughly with distilled water, squeeze out excess water and dry to constant weight in a vacuum oven set at 120°C.
3. After weighing the washed foam, saturate the foam with a 15 percent aqueous oligomer solution by immersing the foam in an 8" x 8" x 3" dish filled with solution.
4. Remove excess oligomer solution by placing the foam piece in a Buchner funnel, covering the funnel with rubber daming and pulling full house vacuum (∿28"Hg). The excess solution is collected in the Buchner flask.
5. Place the oligomer-coated foam into a vacuum oven and hold for 16 hours at 120°C and 28" Hg.

6. Remove the Puramer S-coated foam from the oven, cool in a desiccator and weigh to determine the amount of Puramer S.

7. $\% \text{ Puramer S} = \frac{\text{Wt. of Coated Foam} - \text{Wt. of Foam}}{\text{Wt. of Coated Foam}} \times 100$

8. Cut out 1-inch x 1/4-inch plugs of Puramer S-polyurethane foam adsorbent using a No. 4 cork borer.

9. Place two 1-inch plugs into a 3" x 1/4" stainless steel tube by carefully pushing one plug into each end of the 3-inch tube. This then is the SO_2 collector device.

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